SYNTHESIS OF CALCIUM POROUS ALGINATE BEADS AND THEIR USE FOR ADSORPTION OF 2-NITROPHENOL FROM AQUEOUS SOLUTIONS

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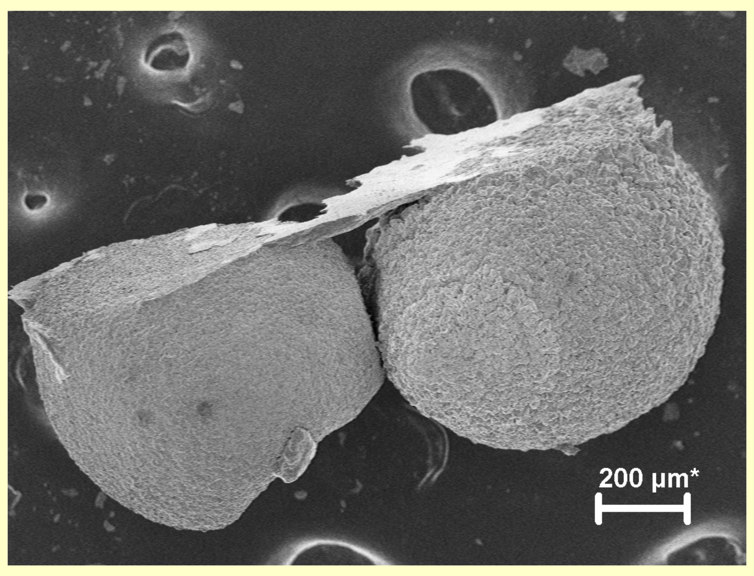
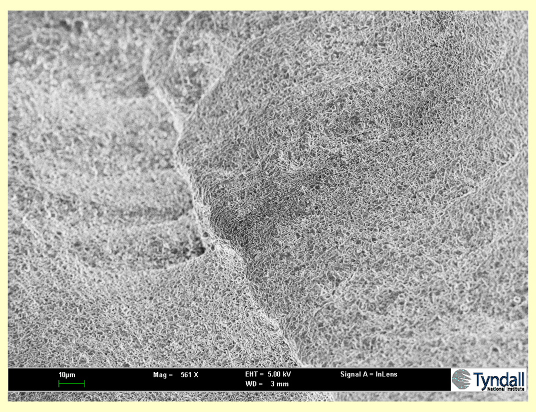
SUMMARY

Alginate is a biopolymer used in recent years to remove cationic pollutants from waste waters [1]. In order to increase the adsorption surface, porous calcium alginate/sodium dodecyl sulfate (SDS) beads were prepared [2]. For the synthesis of the beads, alginic acid sodium salt, SDS as foaming agent, sodium chloride as porogen agent, and calcium chloride ($CaCl_2$) as cross-linker were used. The cross-linking process was studied at different $CaCl_2$ concentrations (1, 5, 10 % wt). The lyophilized samples of calcium alginate/SDS beads were structurally investigated by Fourier Transform Infrared Spectroscopy [3], the pore dimensions and the morphology of calcium alginate matrices were determined by Scanning Electron Microscopy. The calcium porous alginate beads were successfully used to remove the 2-nitrophenol (2-NP) from water. The adsorption of 2-nitrophenol is dependent on pH of the medium, and the adsorption onto calcium alginate/SDS beads reaches a maximum at pH = 7. The sorption and kinetic experiments indicated that the removal efficiency increases with the amount of calcium alginate/SDS beads and decreases with rising of the initial contaminant concentration. The uptake of 2-nitrophenol is rapid in the first 12 hours, and slows down thereafter. The kinetics experiments showed that adsorption 2-nitophenol onto calcium alginate/SDS beads takes place according to the Langmuir model [4].

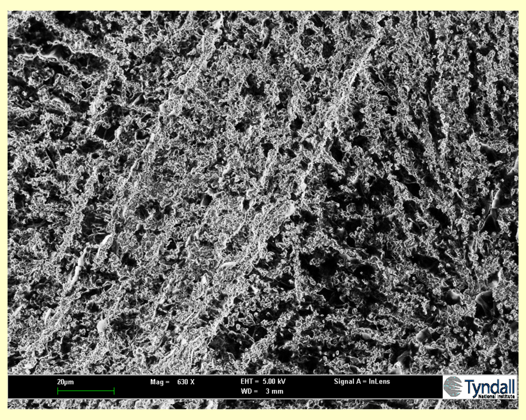
SEM IMAGES



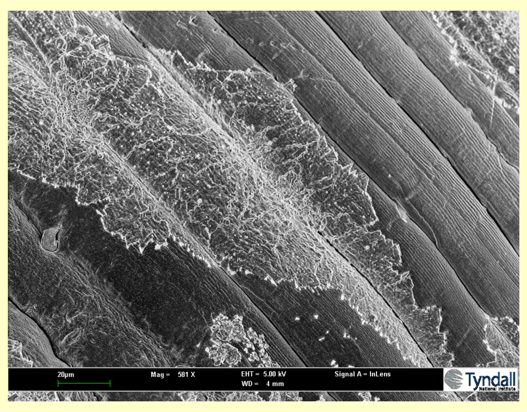
Beads used in the experiments:
CaAlg1-with 1% wt $CaCl_2$
CaAlg2-with 5% wt $CaCl_2$
CaAlg3-with 10% wt $CaCl_2$



Surface porosity of CaAlg-2

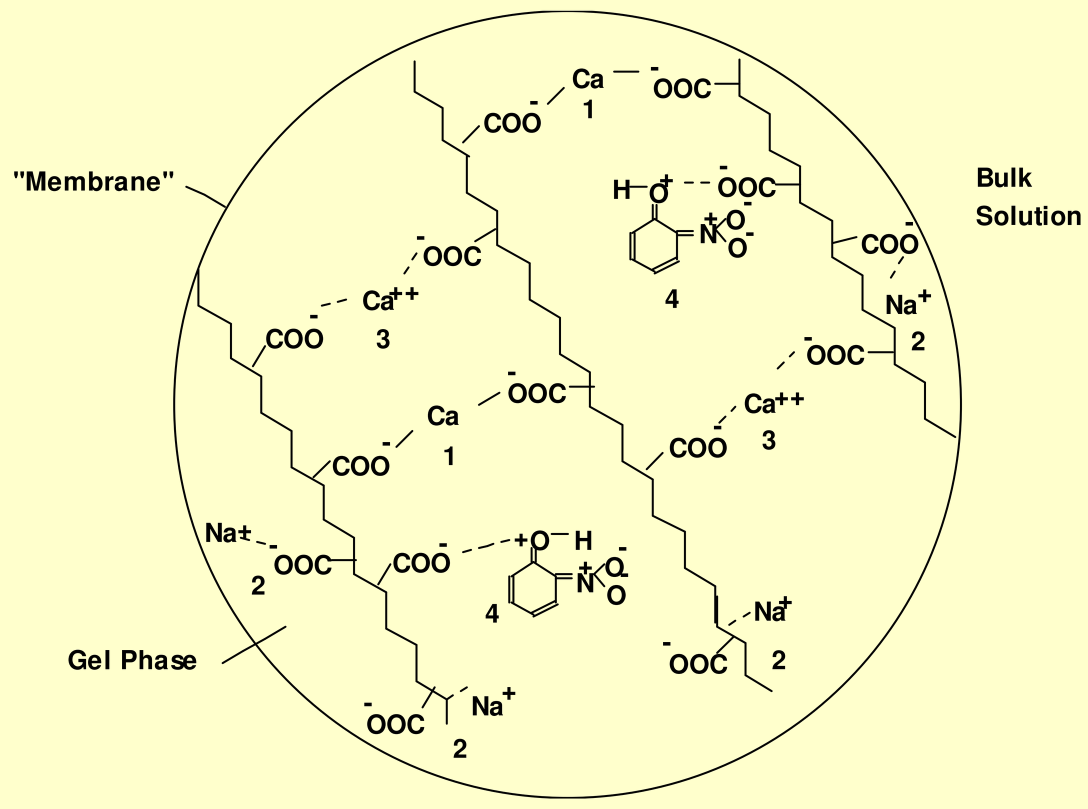


Surface porosity of CaAlg-1



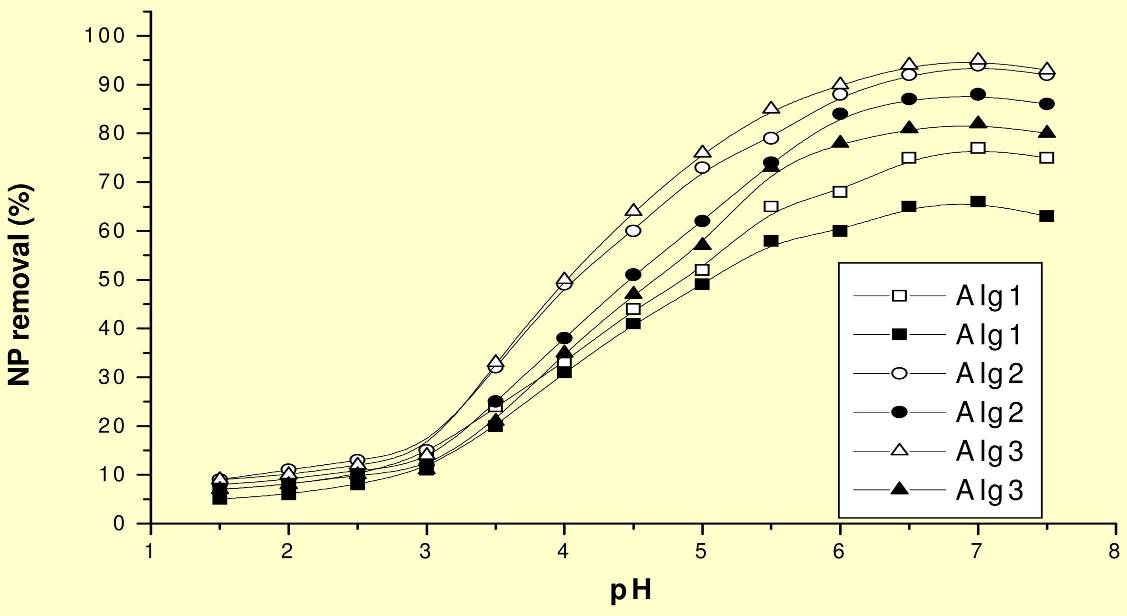
Surface porosity of CaAlg-3

EGG-BOX MODEL



(1) calcium bound; (2) Na^+ that remains in the gel to balance the unoccupied carboxyl groups; (3) free, unbound Ca^{+2} in the gel phase; (4) free, unbound cationic contaminants in the gel phase; dashed lines represent electrostatic interaction between 2-NP and unoccupied carboxyl groups

EFFECT of pH



ADSORPTION MODELS

Langmuir equation

$$q_e = q_{max} K c_e / (1 + K c_e) \quad (1)$$

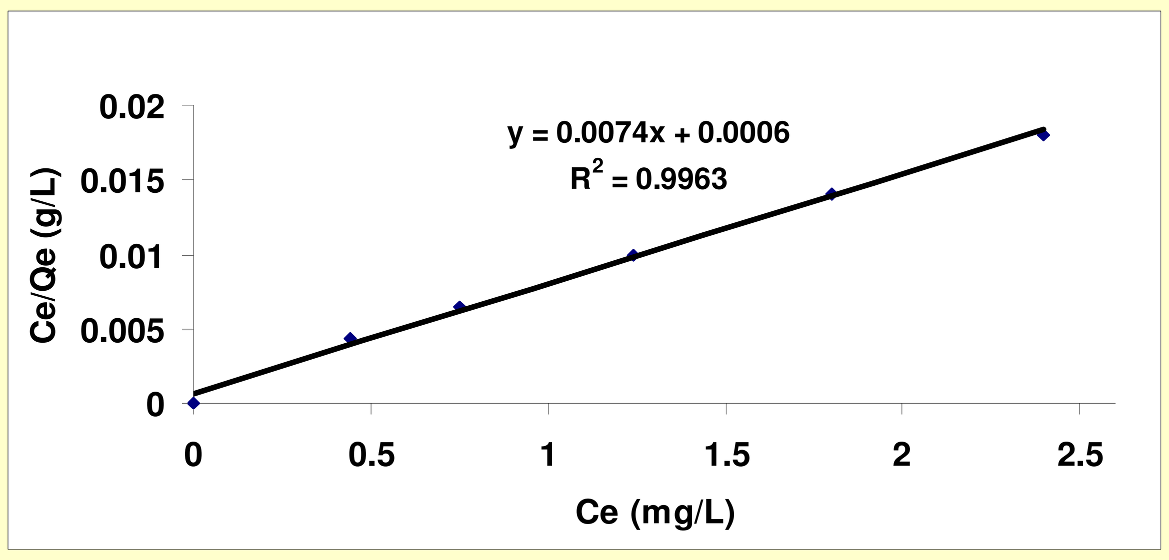
$$c_e/q_e = 1/q_{max}K + c_e/q_{max} \quad (2)$$

Freundlich equation

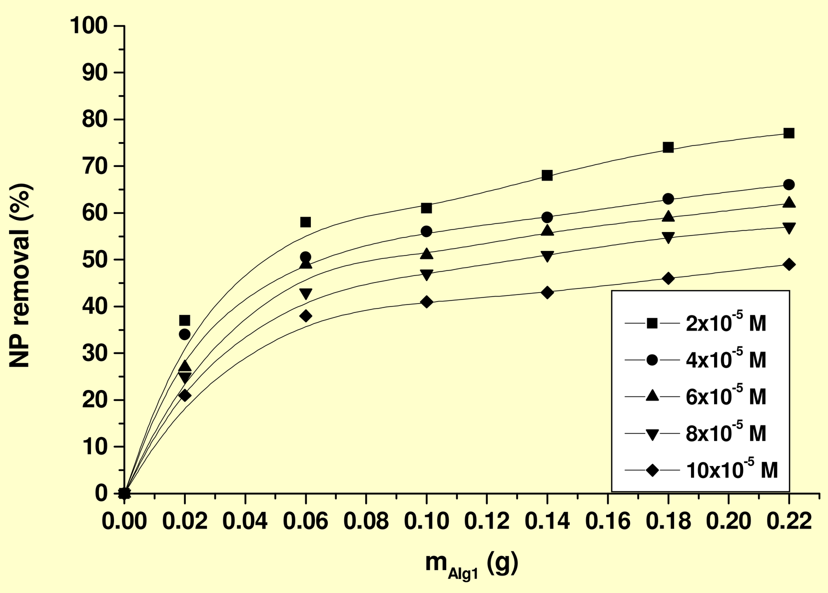
$$q_e = k\, c_e^{1/n} \quad (3)$$

$$\ln q_e = \ln k + 1/n \ln c_e \quad (4)$$

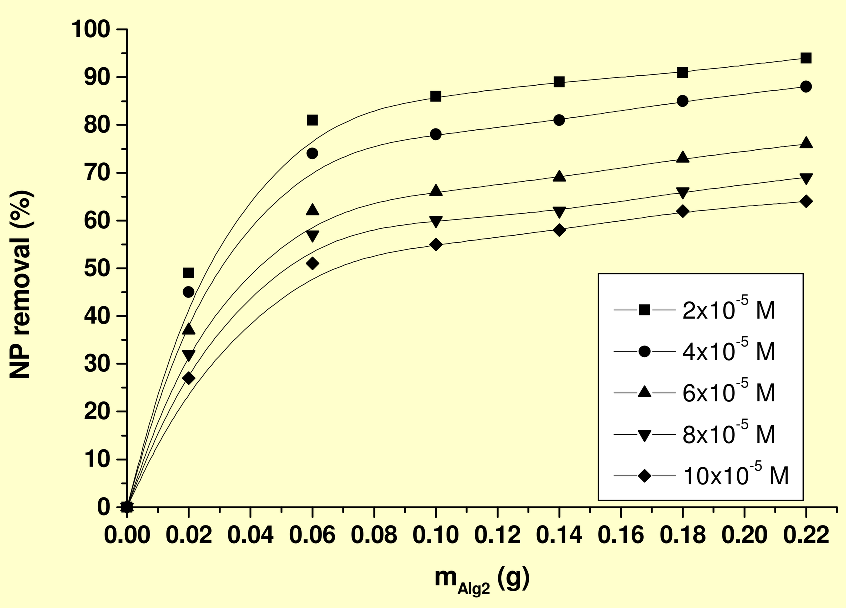
ADSORPTION ISOTHERM



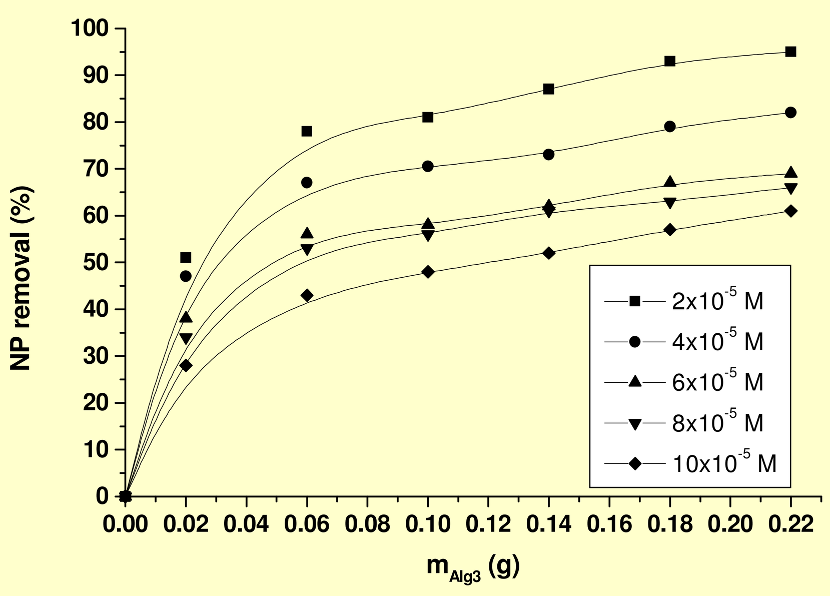
EFFICIENCY of 2-NP REMOVAL



Efficiency of 2-NP removal at different initial pollutant concentration as a function of the amount of Alg-1 beads

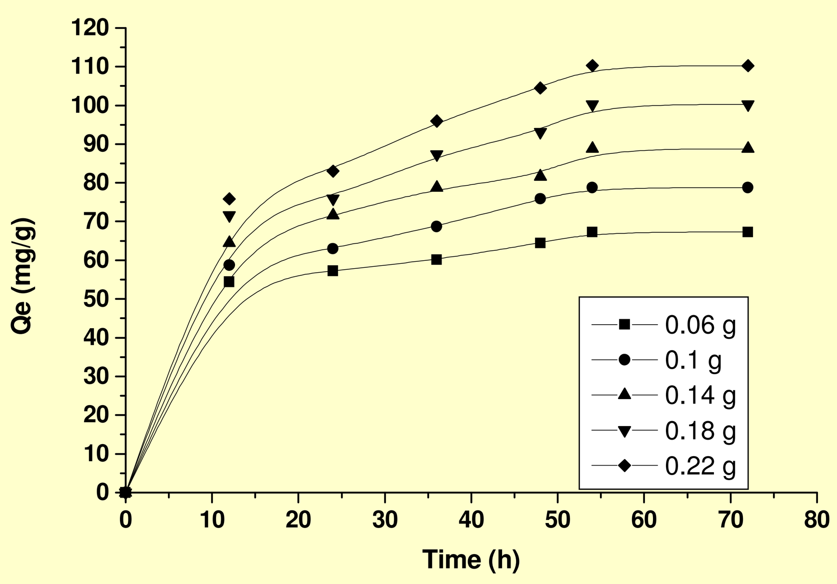


Efficiency of 2-NP removal at different initial pollutant concentration as a function of the amount of Alg-2 beads

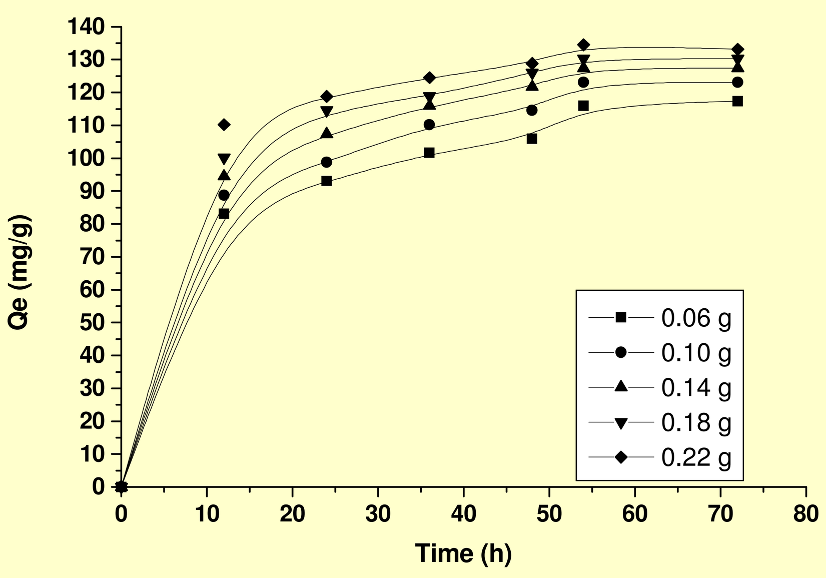


Efficiency of 2-NP removal at different initial pollutant concentration as function of amount of Alg-3 beads

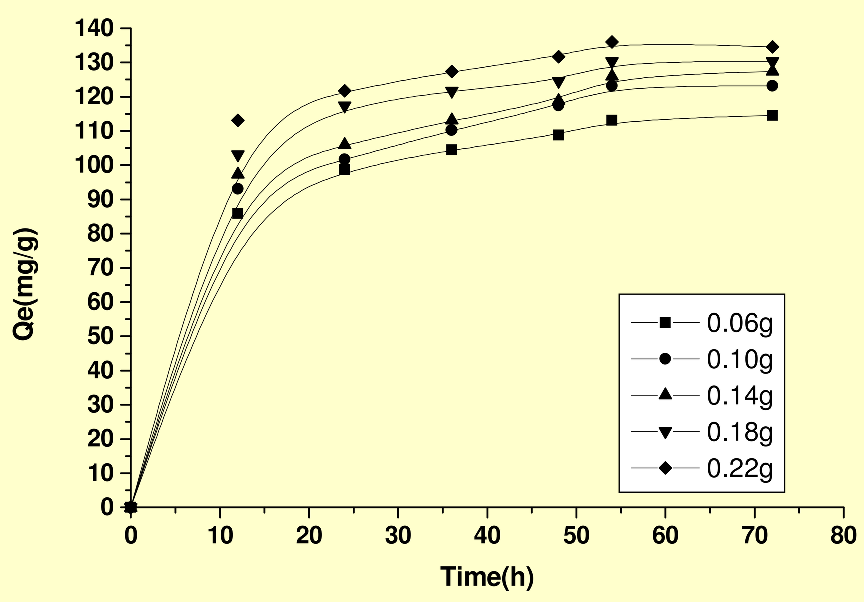
KINETIC EXPERIMENTS



Removal kinetics of 2-NP (C= $2x10^{-5}$M) on different amounts of Alg-1 beads, at pH=7, T= 25 ^{0}C



Removal kinetics of 2-NP (C= $2x10^{-5}$M) on different amounts of Alg-2 beads, at pH=7, T= 25 ^{0}C



Removal kinetics of 2-NP (C= $2x10^{-5}$M) on different amounts of Alg-3 beads, at pH=7, T= 25 ^{0}C

CONCLUSIONS

- Biopolymeric porous beads with a 3-D interconnected pores and lamellar structures were obtained using alginate in the presence of sodium dodecyl sulfate, NaCl as foaming and porogen agents, and $CaCl_2$ as cross-linker.
- The dimension of the pores and the structure of alginate matrices are influenced by the concentration of calcium ions added in the system. SEM data show a variation of pore sizes and morphology by changing the Ca^{2+} concentration.
- FTIR and SEM data reveal that the optimum concentration of $CaCl_2$ for cross-linking the alginate/SDS is of 5 wt %. At 10 wt% $CaCl_2$, the matrix of calcium alginate/SDS is lamellar, being influenced by the self-assembly of the anionic surfactant.
- The experiments show that the 2-nitrophenol derivative is efficiently removed by alginate beads from wastewater.
- The retention efficiency of 2-nitrophenol increases with increasing the amount of calcium alginate/SDS beads, and decreases with increasing of initial pollutant concentration.
- The kinetics of 2-nitrophenol removal has three stages. The first is rapid and removes up to 75% of the pollutant. The second and the third are slow, and remove 94-95 % of the initial amount of 2-nitrophenol.
- The adsorption of 2-nitrophenol onto calcium alginate/SDS beads obeys the Longmuir isotherm.

References

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4. Wu Y., Zhang S., Guo X., Huang H., *Bioresour. Technol.*, 2008, 99, pp.7709–7715.

Acknowledgements

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